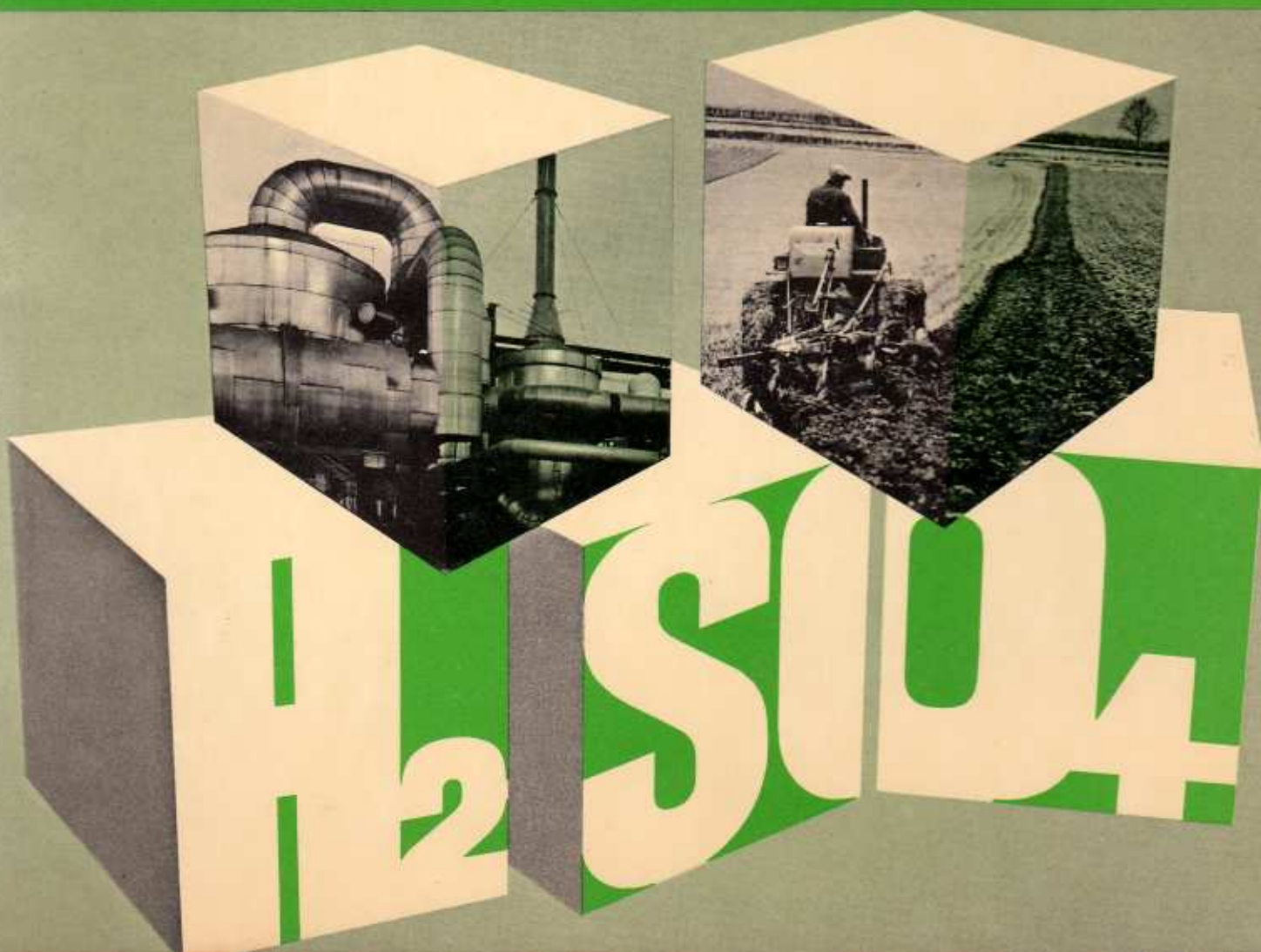
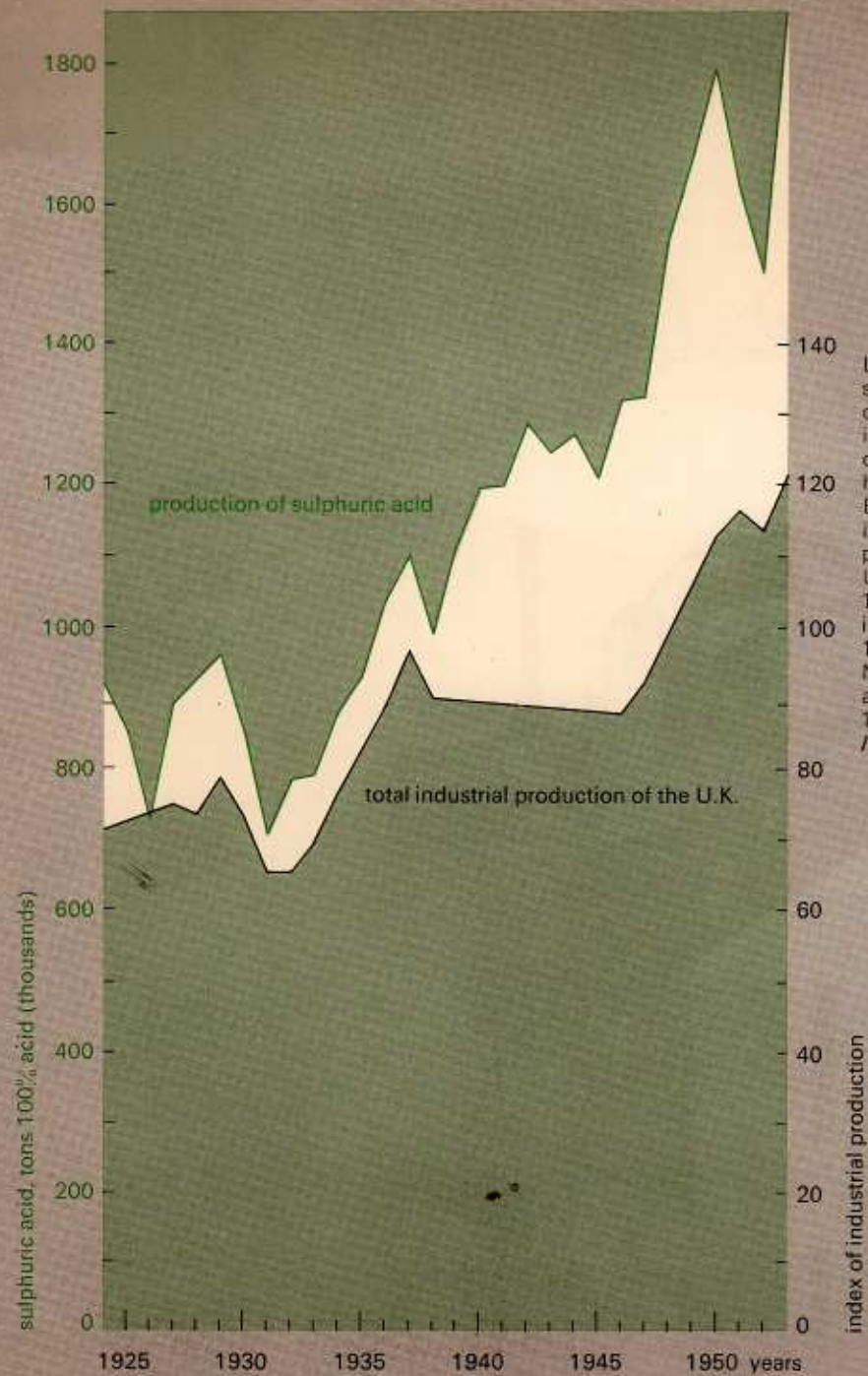




# Sulphuric Acid





Liebig claimed that sulphuric acid consumption was a good indication of a country's commercial prosperity. Shown here is a comparison of British sulphuric acid production in tons with the industrial production index in the United Kingdom for the years 1925-1955. In the industrial index, industrial production in 1948 is arbitrarily taken as 100. No industrial figures are available for the war years 1939-1945.  
I.C.I.



## Part 1

# A history

The importance of sulphuric acid to industry and modern technology was summed up by Liebig over a hundred years ago: 'It is no exaggeration to say that we may fairly judge of the commercial prosperity of a country from the amount of sulphuric acid it consumes.'

For Liebig in the mid-nineteenth century sulphuric acid was an index of technological development. Since his time, many new industries which do not use sulphuric acid have developed to mammoth proportions, while others, like the bleaching and hydrochloric acid manufacturers, have replaced sulphuric acid with other materials. Nevertheless, as we shall see later on when we look at present-day uses, sulphuric acid continues to be a crucial material in many industries. Dye, rayon, detergent and, above all, fertilizer manufacturing are dependent on it. If the consumption of sulphuric acid is no longer a perfect yardstick of industrial prosperity, sulphuric acid continues to be a key material in many important industries.

Little information has come down to us about how or when sulphuric acid was first made. There is some dispute among historians whether the Egyptians were using it by 2500 B.C. to make nitric acid with which they dissolved silver. The first clear account of its preparation dates from about A.D. 900 in Baghdad. Here Al-Razi, a distinguished scholar and alchemist, referred to it in one of his alchemical works.

Al-Razi was a great scholar with an insatiable thirst for knowledge. 'My love and my passion for knowledge, and my labours to acquire the same,' he wrote, 'are familiar to all who have kept my company. . . . If ever I have come upon a book I have not read or heard tell of a man I have not met, I have not turned aside to any engagement whatever – even though it has been to my great loss – before mastering that book or

learning all that man knew.' In his youth, Al-Razi was well known as a poet and musician. When he was thirty years old he decided to devote himself to theology and science. He became one of the most productive scientists of his day. Chemical encyclopedias, theological treatises, biological encyclopedias, geological encyclopedias – scores of volumes are attributed to him.

In one of these volumes, the *Secret of Secrets*, Al-Razi explained what materials, equipment, and procedures were necessary to turn base metals into gold. Here he described how sulphuric acid was distilled from green vitriol. We find no record of its use amongst the Arabs other than in alchemy.

What is most striking is that this first mention of sulphuric acid occurs in an era of intense scholarly activity. Ninth-century Baghdad was the world's greatest centre of commerce and industry. It was the capital of a vast empire that stretched from Spain to what is now Pakistan. Above all, it was the spiritual centre of the Mohammedan religion. Theologians, scholars, philosophers flocked from all over the world to Baghdad to study Muslim theology. Scholars devoted themselves to organizing not only theological thought but any subject matter which lent itself to reasoned exposition. Greek, Syrian and Persian scientific writings were translated and codified. To these were added the Arabs' original work. Elaborate histories were written, as well as works on biology, agriculture, mechanics, irrigation and engineering. Advances in algebra, analytical geometry and trigonometry gave us our present-day definitions of sine, cosine, and tangent, and the word 'algebra' itself.

Al-Razi's reference to sulphuric acid marks its entrance into the realm of learned writings. Within this realm, the instructions for its preparation were transmitted to Europe



after the eleventh century, along with many other Greek and Arab writings. Robert of Chester refers to it in one of his translations from the Arabic. After him, both Albertus Magnus and Paracelsus mention it. Van Helmont (1577–1644) seems to have been well acquainted with it. He refers to two methods of making it: by heating green vitriol (iron [II] sulphate); and by burning sulphur under a glass bell. Both these methods coexisted throughout the sixteenth and seventeenth centuries. John Glauber writing in the middle of the seventeenth century gave perhaps the most vivid description of the green vitriol method.

‘Commonly in all fat soils or clayey grounds, especially in the white, there is found a kind of stones, round or oval in form . . . Which if it is cleansed from the earth, and beaten to pieces, looks within of a fair yellow and in streaks, like a gold Marcasite, or a rich gold Ore, but there is no other taste to be perceived in it, than in another ordinary stone; . . . Now this stone is nothing else, but the best and purest Mineral (or Ore) of Vitriol, . . . out of which there may be made an excellent medicine, as followeth.

‘Take this Ore or Mineral beaten into pieces, and for some space of time, lay or expose it to the cool air, and within the twenty or thirty days it will magnetically attract a certain saltish moisture out of the air, and grow heavy by it, and at last it falleth asunder to a black powder, which must remain further lying there still, until it grow whitish, and that it do taste sweet upon the tongue like vitriol. Afterward put it in a glass vessel, and pour on so much fair rainwater, as that it cover it one or two inches; stir it about several times in a day, and after a few days the water will be coloured green, which you must pour off, and pour on more fair water, and proceed as before, stirring it often, until that also come to be green: this must be repeated so often, until no water more will be coloured by standing upon it. Then let all the green waters which you poured off run through filtering paper, for to purify them; and then in a glass-body cut off short let them evaporate till a skin appear at the top: then set it in a cold place, and there will shoot little green stones, which are nothing else but a pure vitriol: the remaining green water will evaporate again, and let it shoot as before: and this evaporating and crystallizing must be continued until no vitriol more will shoot.’ These ‘green’ stones were heated, and the resultant liquid was distilled into sulphuric acid.



Johann Baptista van Helmont  
1577 – 1644.  
Ronan Picture Library.





Sixteenth-century apparatus for making sulphuric acid from green vitriol.

In modern terms, the prolonged heating of iron (II) sulphate crystals drove off the water of crystallization. The iron (II) sulphate decomposed to give oxides of sulphur which were then absorbed into the vaporous water of crystallization to form sulphuric acid, which could then be concentrated by distilling away the water.

The other method of making sulphuric acid which was known to van Helmont was equally inefficient. Pure sulphur was burnt under a glass globe until it stopped burning. Then more sulphur was added and burnt. In this way the sulphur was oxidized and combined with the moisture in the air under the globe to form sulphuric acid. This latter method was vastly improved by the addition of a nitre catalyst and of 'moist air', air with higher water content with which the oxidized sulphur could combine. In 1690 Nicholas Lemery developed a still more efficient method. He burned sulphur and nitre (potassium nitrate) in a glass globe and collected the vapours in a large pot of water. As more and more batches of sulphur were burned, the sulphuric acid forming in the pot of water became more and more concentrated. This method was much more efficient. Its refinement led to the great industrial development of sulphuric manufacturing in the following century.

Unfortunately, not very much is known about the traditional uses of sulphuric acid, apart from the alchemical use already mentioned. In the seventeenth century it was used in pharmacy for making Glauber's 'sal mirabile'. This was prepared by adding sulphuric acid to common salt. Miraculous curative powers were attributed to the resultant sodium sulphate. Sulphuric acid was also used in combination with lime to make gypsum; and it was used, as we have said, from very early times to make nitric acid for dissolving silver.

Burning sulphur for the manufacture of sulphuric acid by the glass bell method.  
*Science Museum, London.*





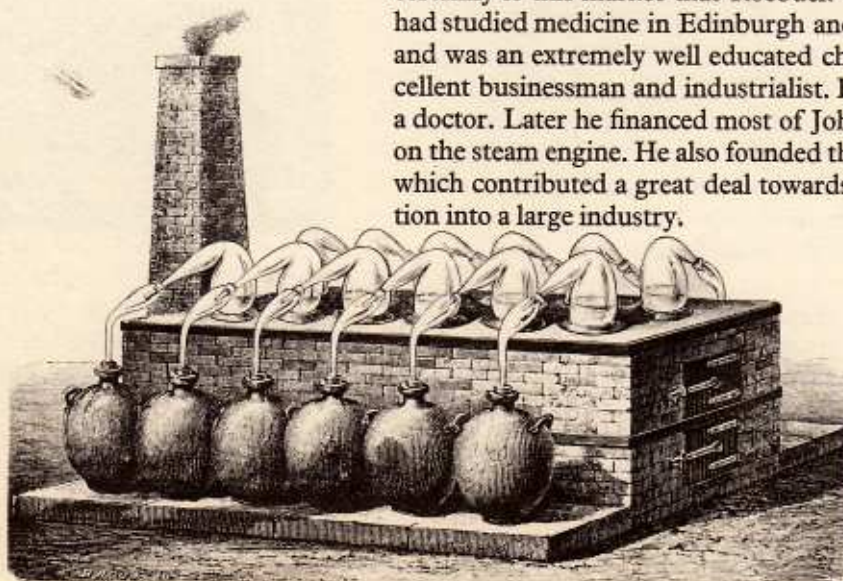


One of the traditional uses for sulphuric acid was in pickling metals. Here is an eighteenth-century buttonmaker's workshop where metals were used for making buttons.

*Ronan Picture Library.*

An apparatus similar to Joshua Ward's for concentrating sulphuric acid. Ward's method survived on a very small scale up to the beginning of the twentieth century.

*Ronan Picture Library.*



There are good indications that it was used in the early eighteenth century in tin-plate making, brass founding, button manufacture, and refining precious metals. It was used either to clean metals or to remove copper from silver. And it was used to make dyes for textiles.

It was certainly to appeal to a market of this sort that Joshua Ward began the first large-scale venture in sulphuric acid manufacture in 1736 at Twickenham. He used a sodium nitrate catalyst instead of potassium nitrate, which was more expensive. At the Twickenham factory he burned sulphur in sixty-gallon glass globes. With production going on in 100 of these globes at once, he produced a large enough quantity to lower considerably the price of sulphuric acid. Ward's venture seems to have achieved fair success. But from the point of view of chemical history, it was more a business venture than a feat of chemical engineering. The Twickenham factory and its successor in Richmond (Surrey) amounted to little more than a big laboratory. Ward produced acid in large enough quantities to reduce the price but not in a way that exploited industrial conditions.

The transplantation of sulphuric manufacture from the laboratory to the factory occurred very soon afterwards. In 1746 Dr John Roebuck set up a new factory in Birmingham. Here was a large metal trade to buy sulphuric acid, and it was certainly to this market that Roebuck wanted to appeal. He had studied medicine in Edinburgh and Leyden, in Holland, and was an extremely well educated chemist and also an excellent businessman and industrialist. He began his career as a doctor. Later he financed most of John Watt's experiments on the steam engine. He also founded the Carron Iron Works, which contributed a great deal towards making iron production into a large industry.



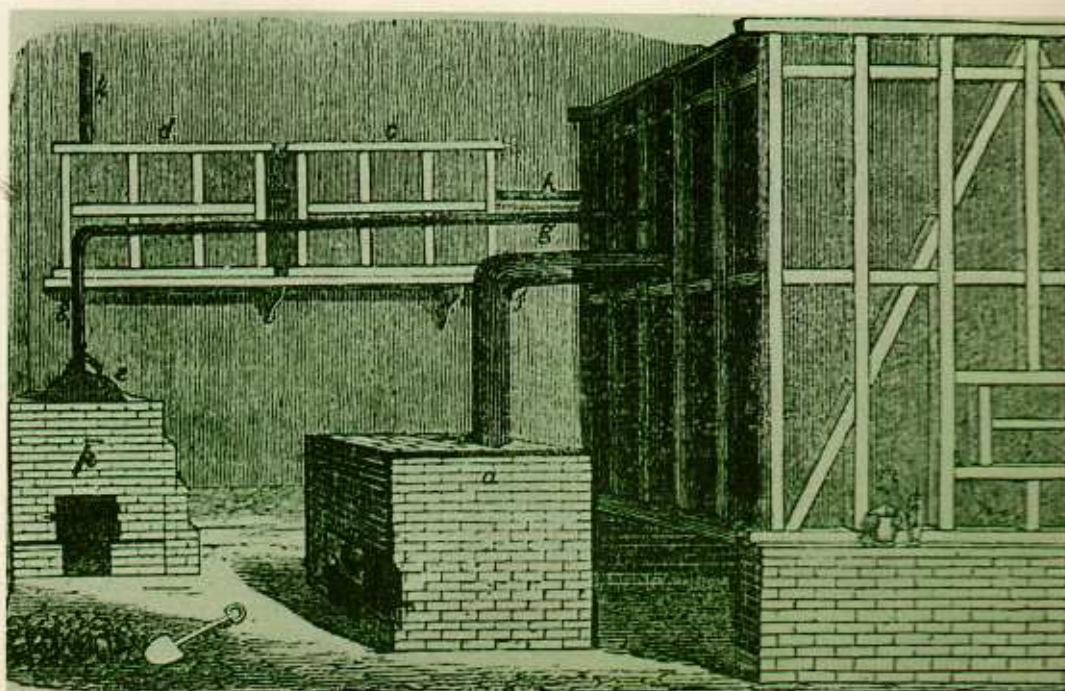
In the course of his studies, Roebuck had strayed across Glauber's observation that sulphuric acid does not attack lead. With lead he could make a single large chamber to produce as much acid as several dozen of Joshua Ward's glass globes. After the success of his first factory in Birmingham he set up his second factory in Prestonpans on the Firth of Forth in Scotland. Here much of the sulphuric acid was used in a new process for bleaching linen. A description of one of the lead chambers reveals how completely it transformed sulphuric production into a factory process: 'They were ten feet square and twelve feet high with a roof like a cottage, each house having a door, usually of mahogany, and a valve on top for ventilation between burnings. The floor was constructed to hold water to a depth of eight or nine inches. The 1 lb charge, consisting of a mixture of seven to eight parts of sulphur with one of nitre, was introduced upon two trays. This was lit and the doors shut for upwards of an hour until the combustion had taken place. Three hours from the time of lighting were allowed for condensation to take place, after which the doors and valve were opened to 'sweeten the chamber'.

This operation was repeated every four hours, day and night, for about two weeks until the acid which accumulated on the floor of the chamber was strong enough. Then the acid was run off and stored in lead vessels.

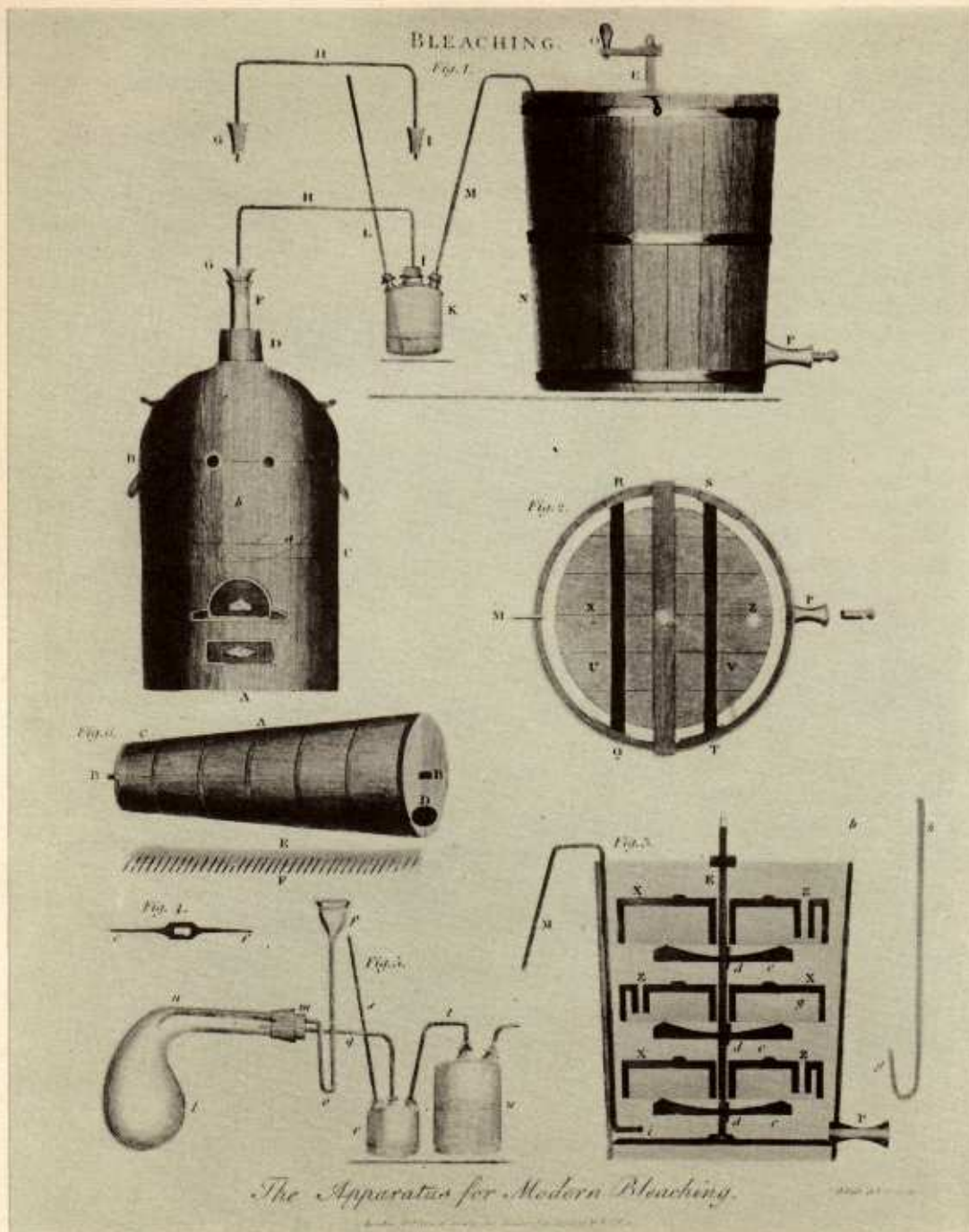
The progress of sulphuric acid, from its first very inefficient production to its use by Arab and medieval European alchemists, to scholarly writings on alchemy, and, ultimately, to the factory, is typical of a great many chemical substances. Each age seems to have fitted its chemistry into the slot provided by the chief interests of its time. For Al-Razi sulphuric acid was in some sense an entry in an encyclopedia with potential use in the laboratory. For van Helmont it was a substance whose production the chemist could explore. For Ward and Roebuck it was a business venture. Since their time it has been of vast technological significance.

As the industrial revolution proceeded more and more uses were found for cheap acid. When chlorine bleaches were introduced into the bleaching industry, sulphuric acid was used to make chlorine. Dyers used it in preparing dyes. By 1820 there were some forty sulphuric factories in Great Britain alone.

An early lead chamber process used shortly after the introduction of a continuous flow system of manufacture. The sulphur and the catalyst were prepared in the kilns (a,e); c and d and the large structure on the right are lead chambers.  
*Ronan Picture Library.*







The largest boost to the eighteenth-century sulphuric industry came from the development of a bleaching method in which sulphuric acid was used. At the end of the century chlorine bleaches were developed. These were also made with sulphuric acid and used in an apparatus such as the one shown here. *Radio Times Hulton Picture Library.*



Louis Joseph Gay-Lussac,  
1778 – 1850.  
*Radio Times Hulton Picture Library.*





Gypsum manufacture was another of the traditional uses for sulphuric acid.  
*Radio Times Hulton Picture Library.*

Simultaneously improvements were introduced into the manufacturing process. Some of these were based on advancements in chemists' understanding of exactly what was happening in the lead chambers. Roebuck's method produced only an intermittent supply of the acid after days of burning sulphur and gradually concentrating the acid that accumulated on the floor of the chamber. Subsequent improvements aimed at making the flow continuous, at eliminating impurities, and at hastening the process.

In 1793 Clément-Desormes showed that the action of the nitrogen dioxide catalyst was hastened by letting a stream of air into the chamber. About 1803 a continuous process came into use: sulphur was burned outside the lead chambers and the resultant sulphur dioxide was fed into them in a continuous flow. One of the problems with the early lead chamber processes was that the nitrogen dioxide catalyst was released into the air and became a nuisance to the people who lived in the surrounding area. In 1827 Gay-Lussac invented a tower to reabsorb the nitrogen oxides that came out of the lead chambers. It was not until 1859 that a method was devised by John Glover to recover the nitrogen oxides from the Gay-Lussac tower and use them again in the lead chambers, so saving the cost of the catalyst.

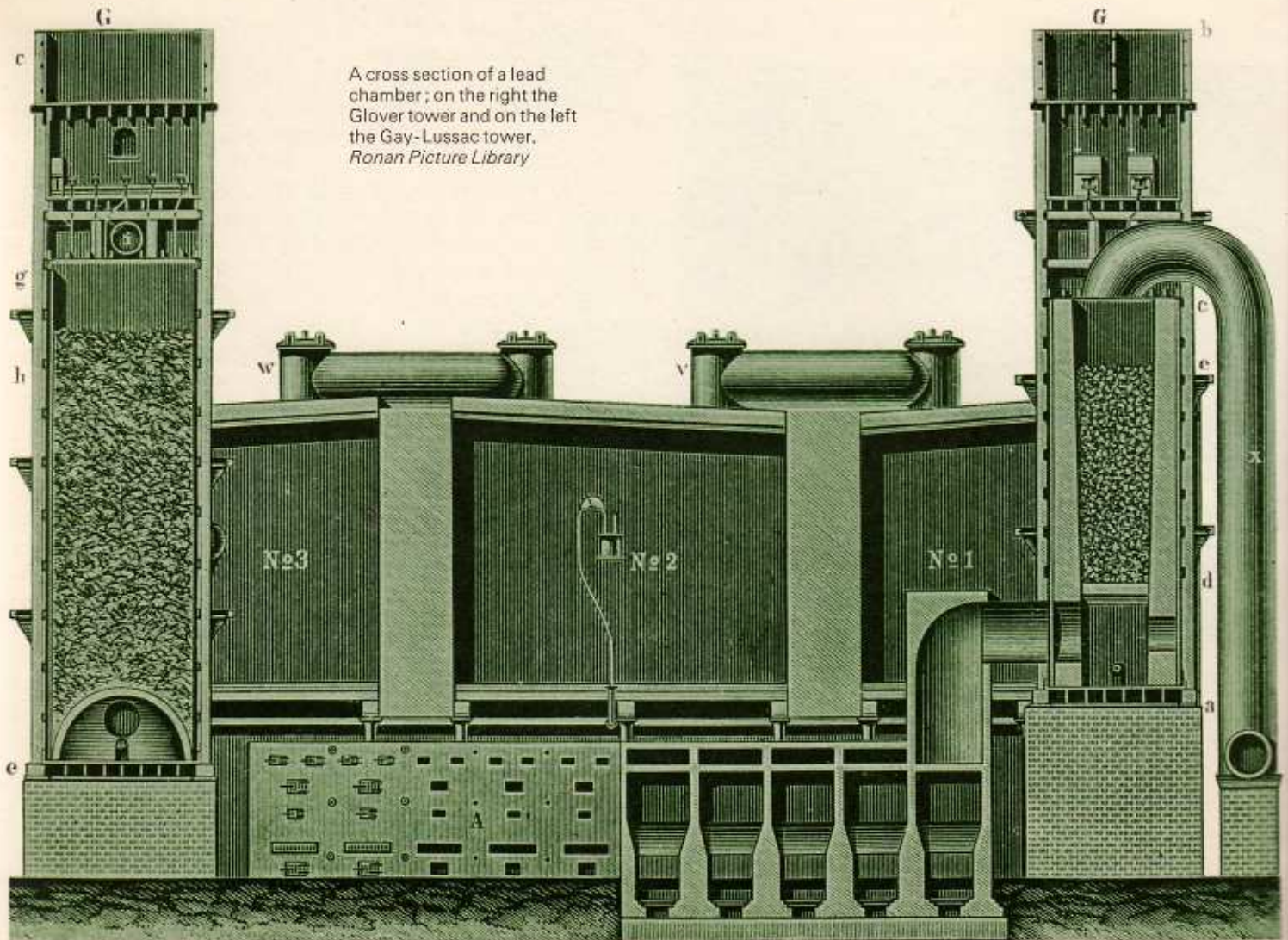
As we examine present-day manufacturing processes, and find out how sulphuric acid is used, we shall see that today's procedures amount to a refinement and a simplification of the procedures we have just examined. For example, the lead chamber process, even after it was made continuous, still required that the sulphur dioxide be oxidized to sulphur trioxide in the same chamber in which the sulphur trioxide combined with water to form sulphuric acid. The development of a more efficient catalyst allowed for these two steps to be separated.

In 1831 Peregrine Phillips took out a patent for a process which used a platinum catalyst. The sulphur dioxide was oxidized in the presence of this catalyst, and the resultant sulphur trioxide was dissolved directly in previously prepared sulphuric acid. The resulting solution could be diluted with water as the consumer required. This new process was called the contact process. Although it was accepted only very slowly by manufacturers, most acid is today made in this way, chiefly because the process is simpler and more easily and more accurately controlled than the chamber process.



## Part 2

# Manufacture





In the contact process and the lead chamber process, the same general pattern is followed: sulphur dioxide ( $\text{SO}_2$ ) is oxidized to sulphur trioxide ( $\text{SO}_3$ ), which then combines with water to form sulphuric acid ( $\text{H}_2\text{SO}_4$ ). Both processes require a catalyst: the lead chamber process uses gaseous nitrogen dioxide as a catalyst, while the contact process uses a solid platinum catalyst, or more recently, vanadium pentoxide.

*The lead chamber process* — In present-day chamber plants, a continuous flow system is used. Before the sulphur enters the sulphuric plant, it is burned to form sulphur dioxide. The sulphur dioxide, at a temperature of about  $600^\circ\text{C}$ , is then fed directly into the Glover tower. As it passes from the bottom to the top of the Glover tower, it meets a stream of sulphuric acid flowing down from the top. We shall see in a moment that this acid comes from the Gay-Lussac tower at the other end of the chamber process. It contains the dissolved nitrogen dioxide catalyst which escapes from the lead chamber after the sulphuric acid is formed. In the Gay-Lussac tower, the catalyst is dissolved in cold sulphuric acid. It circulates back to the Glover tower, where the incoming sulphur dioxide raises its temperature and the dissolved nitrogen dioxide is released.

The mixture of sulphur dioxide and nitrogen dioxide passes up to the top of the Glover tower. The gases must be cooled before they enter the lead chamber so as to produce the best results. When the sulphur dioxide enters the Glover tower just after burning its temperature is about  $600^\circ\text{C}$ . When the mixture of sulphur dioxide and nitrogen dioxide leaves the Glover tower its temperature has been lowered to  $90^\circ\text{C}$ .

From the Glover tower, the gases pass into the lead chambers. Inside the chambers a fine spray of air and water showers down from above. Sulphur dioxide combines with oxygen and water to form sulphuric acid. This action would take place very slowly if nitrogen dioxide were not present. Nitrogen dioxide gives up oxygen to sulphur dioxide, forming sulphur trioxide, which then combines with the water to form sulphuric acid. The nitrogen dioxide then takes back its oxygen from the air in the chamber. Temperatures are kept as low as possible to help the sulphuric acid condense. For this reason, there are often cooling systems around the lead chambers to absorb the large amount of heat given off by the oxidation of sulphur dioxide. Usually there are several chambers, one after the other. The sulphur dioxide passes through three or four chambers before all of it has combined to form sulphuric acid.

Sulphuric acid flows out from the bottom of the chambers. It is packed and stored until an order for it arrives from a consumer. The nitrogen oxides, free nitrogen from the air, and remaining undissolved sulphur dioxide are fed into the bottom of the Gay-Lussac tower. Here they meet a stream of cold sulphuric acid. The acid dissolves the gases and is pumped back again to the top of the Glover tower. As it flows down the Glover tower it meets the inflowing hot sulphur dioxide. The temperature of the acid rises and the nitrogen oxide escapes from the sulphuric acid. It joins the sulphur dioxide and the mixture is cooled and passes on to the lead chambers.

Not all of the nitrogen dioxide can be recovered, since some of it dissolves in the sulphuric acid leaving the plant. Small amounts of it have to be added to the gases entering the chamber. Sodium nitrate, the old source of nitrogen dioxide,





Sulphuric acid is generally transported in lead tanks.  
Laporte Industries Ltd.

has recently been replaced by ammonia, which is catalytically oxidized to form nitrogen dioxide.

What is most important about the lead chamber process is that incoming sulphur dioxide does not have to be perfectly pure. Any raw material which contains sulphur dioxide can be used, since impurities do not generally decrease sulphuric acid formation and have little adverse effect on the nitrogen dioxide catalyst. For this reason, sulphuric acid from lead chambers is cheaper than acid made by the contact process.

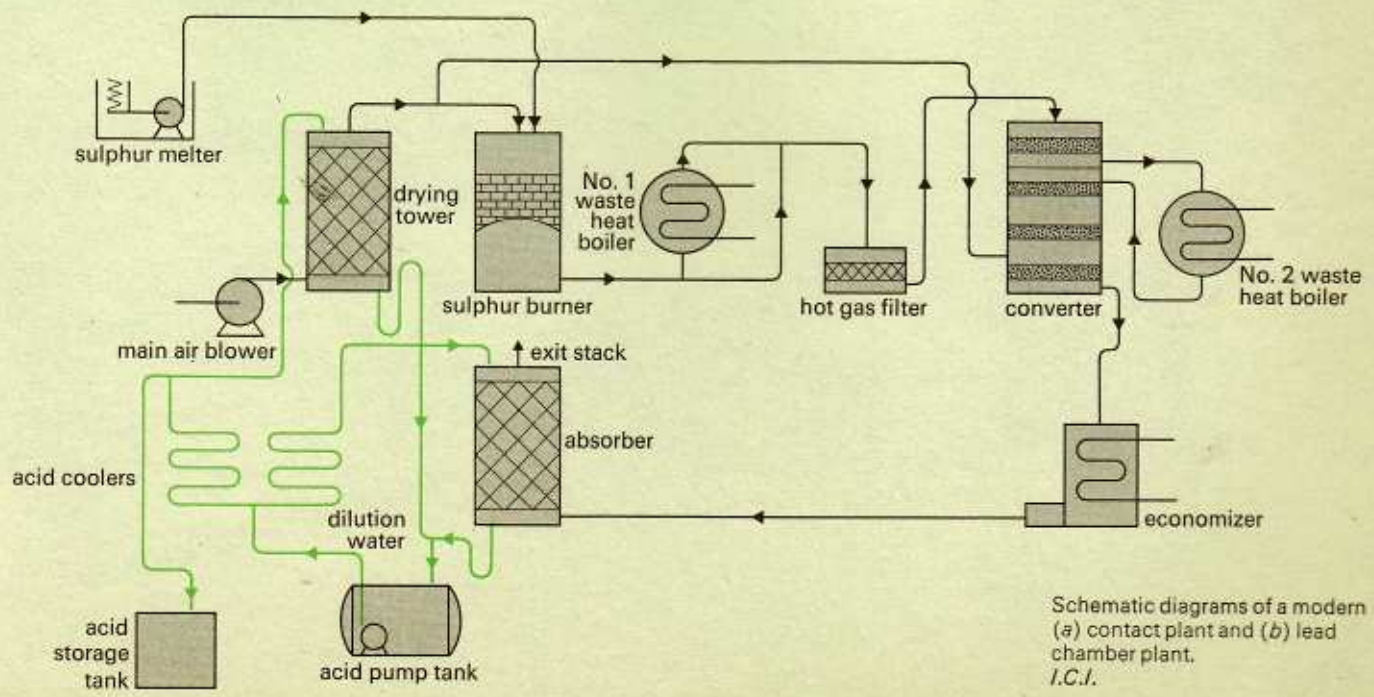
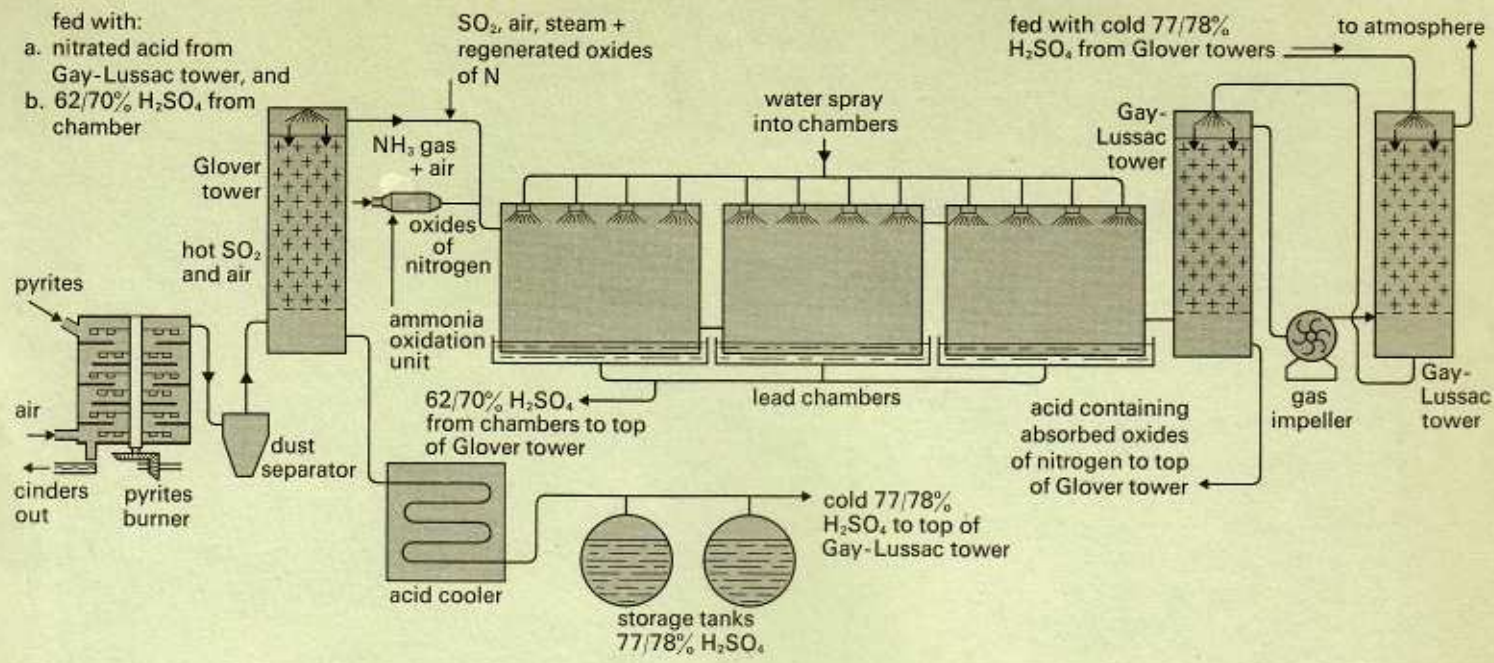
It is difficult, however, to regulate the concentration of sulphuric acid leaving the chambers: regulation not only involves perfect control of the ratios of sulphur dioxide, nitrogen dioxide, water, air, and oxygen, it also involves careful control of temperatures and of the time the various substances are left in contact with each other. Furthermore, very strong sulphuric acid does attack lead. The upper ranges of concentration have to be avoided if the chambers themselves are to be used for a long time. Very concentrated sulphuric acid also dissolves nitrogen dioxide more readily than weaker concentrations. Dilution is essential if the nitrogen dioxide is to be released into the Gay-Lussac tower and absorbed to be used again.

Thus the chamber process is designed to produce 62 or 70 per cent sulphuric acid. This is generally used in production of fertilizers. Fertilizers are all the better if they contain nitrogen from the nitrogen oxides dissolved in chamber acid. The small quantities of lead inevitably dissolved in the chamber are not enough to affect plants on which fertilizers are used.

*The contact process* – In the contact process, the concentration of the finished product can be very accurately regulated, but the sulphur dioxide has to be very pure. Impurities which are not removed 'poison' the catalyst and vastly increase production costs. It is therefore cheaper to remove impurities before the sulphur dioxide reaches the catalyst.

The contact process involves the formation of sulphur trioxide from sulphur dioxide in the presence of a solid metal catalyst. Originally platinum was used as catalyst, but today it has been replaced by vanadium pentoxide, which is considerably less expensive. Sulphur dioxide and air are heated to 400 or 450°C and fed into a converter. Here they are exposed to the vanadium pentoxide catalyst. The sulphur











A sulphur dioxide blower in a contact acid plant.  
*Shell.*

A section of an absorber tower in a contact plant showing the glass absorbers where the sulphur trioxide is absorbed.  
*Laporte Industries Ltd.*



dioxide combines with the oxygen in the air to form sulphur trioxide ( $\text{SO}_3$ ). Usually the sulphur dioxide does not oxidize immediately and it must be fed into a series of converters before all of it has been oxidized. The temperature must be carefully controlled, since the catalyst is most effective between 400 and 450°C.

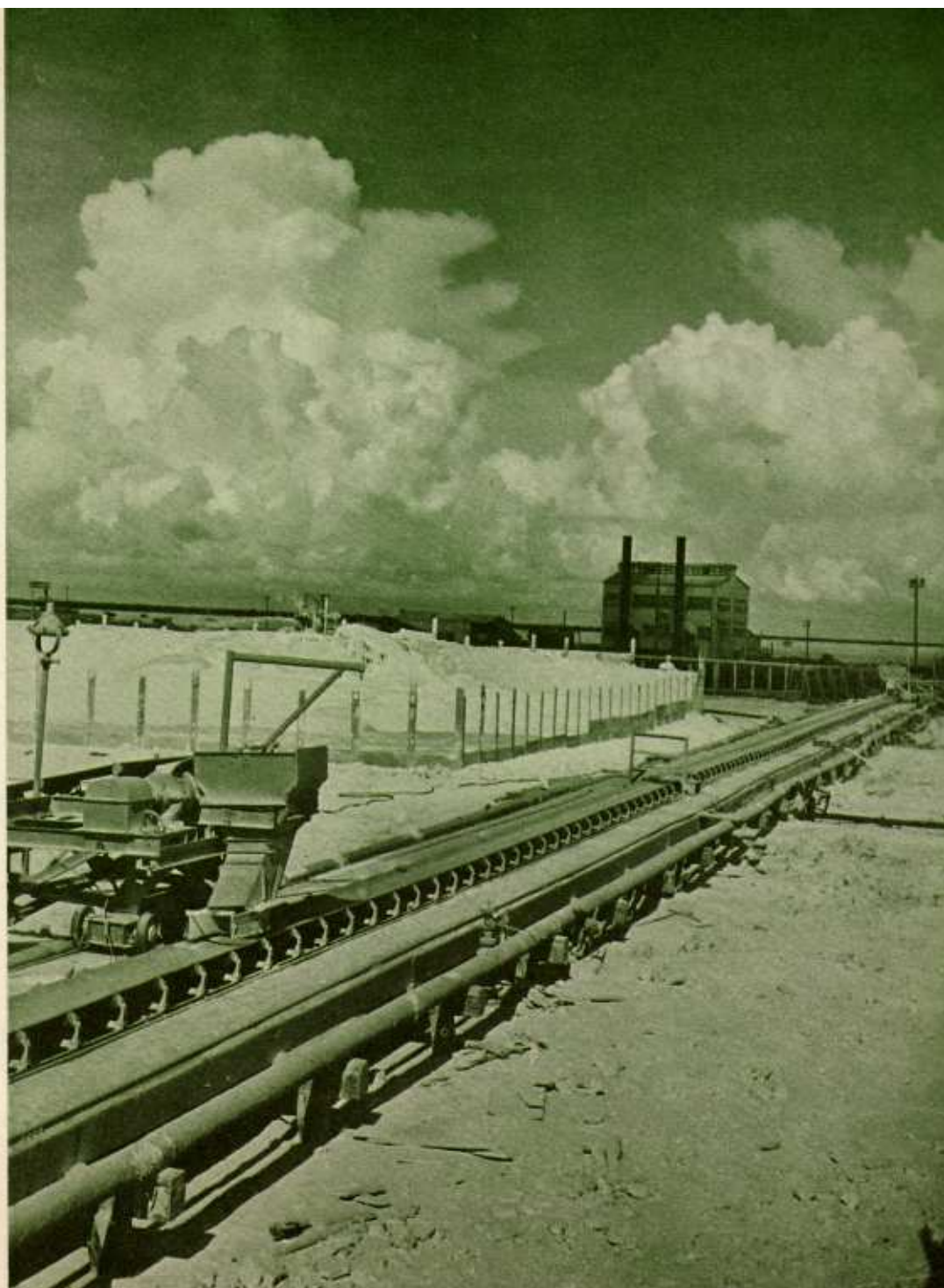
When about 95 per cent of the sulphur dioxide has been oxidized, the resultant sulphur trioxide enters an absorber tower. Here the sulphur trioxide combines with water to form sulphuric acid. Sulphur trioxide, however, does not combine readily with water: it is not soluble in water. When sulphur trioxide is introduced into water only a small part of the sulphur trioxide dissolves. It forms sulphuric acid which reacts violently with the rest of the water. This reaction produces fumes which are hazardous to factory employees. Since sulphur trioxide does dissolve in sulphuric acid, it is fed into the absorber tower to meet a stream of 100 per cent sulphuric acid. This solution of sulphuric acid and sulphur trioxide is called oleum. Since a great many manufacturers use oleum—manufacturers of detergents, for example—oleum is often left intact. Otherwise concentration can be precisely controlled by adding more or less water. Water combines with the sulphur trioxide in the oleum to form more sulphuric acid.

The contact process is really a simplification of the lead chamber process. The catalyst in the contact process was discovered in a search for something better than nitrogen dioxide. The advantage of the contact process is that each phase can be exactly controlled.

In recent years the contact process has gained predominance over the chamber process. Today less than 7 per cent, or only 211,000 tons, of sulphuric acid is made by the lead chamber process. Most manufacturers prefer the contact process because they can produce acid exactly to the specifications required.



The sulphur mine at the Freeport Sulphur Company in Louisiana. The molten sulphur in the background is left to dry and solidify; then it is cut into blocks for shipping.  
*Radio Times Hulton Picture Library.*





## Part 3

# The sources of Sulphur Dioxide

The Frasch process shown here was designed especially to extract sulphur from underground deposits.  
*I.C.I.*

Both the contact process and the lead chamber process make sulphuric acid from sulphur dioxide. Sulphur is found in a number of raw materials: pure sulphur, iron pyrites, spent oxides, zinc sulphide, and anhydrite.

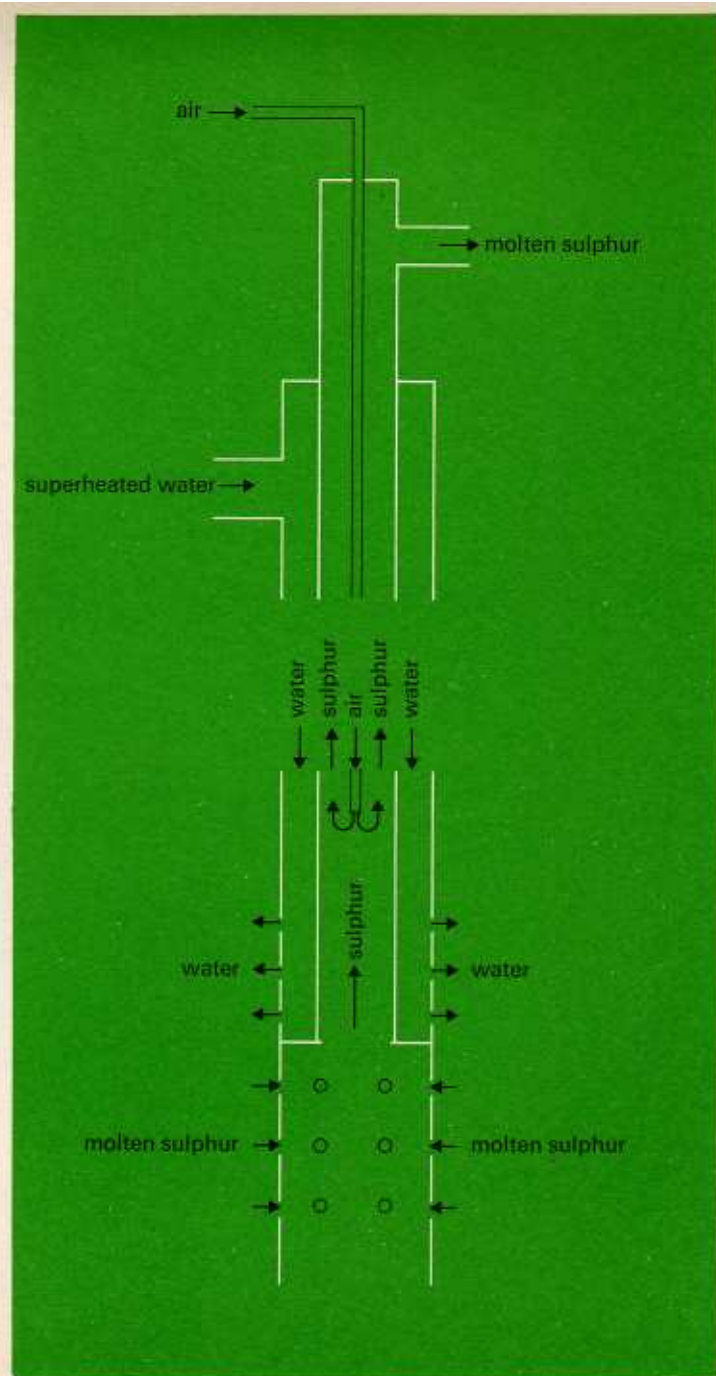
**Sulphur** – In 1868 some oil prospectors in Texas and Louisiana discovered a vast subterranean sulphur deposit. Until this time, Sicily had been the main supplier of pure sulphur. Because it was difficult to work, this deposit was not mined until 1890, when the Frasch process was developed. Superheated water is pumped down to the deposits at some 500 feet below the surface of the ground. The sulphur melts and it is pumped to the surface with the aid of hot compressed air. It is dried into a solid and shipped to various factories.

To make  $\text{SO}_2$ , pure sulphur is simply burned in the presence of air. A minimum of purification is necessary to have sulphur dioxide pure enough for the contact process.

**Iron pyrites** – Iron pyrites is a sulphide of iron ( $\text{FeS}_2$ ). Pyrites ores usually contain about 45 per cent of sulphur. They often contain small quantities of copper, silver, and gold. They are mined chiefly in Spain, Norway, and Cyprus.

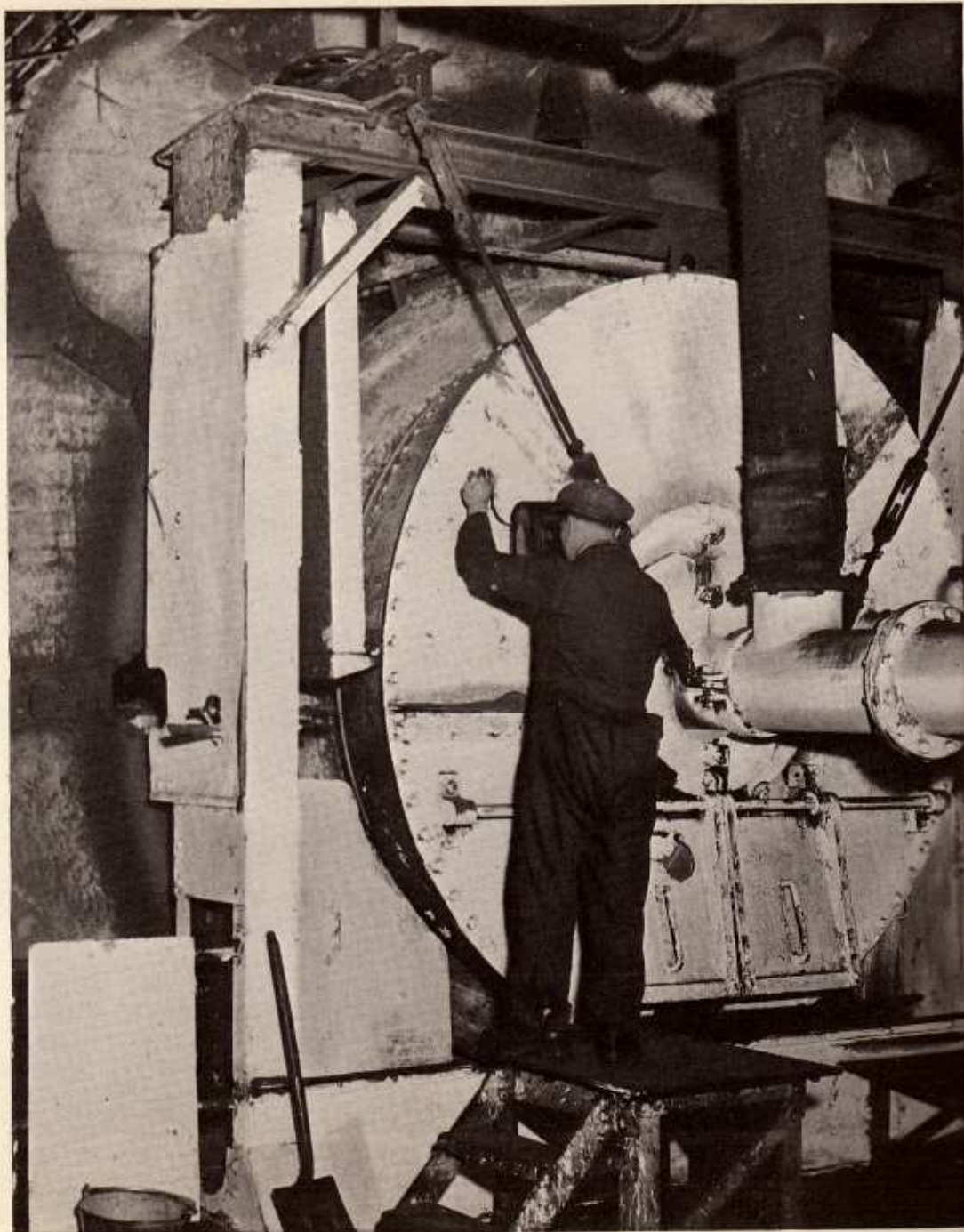
Pyrites is burnt in a furnace or in a kiln. If a furnace is used, the pyrites enters at the top and it drops down along a series of shelves until it reaches the bottom. Usually a set of rakes is used to scrape the pyrites from one shelf so that it can fall to the next. As it descends, the sulphur and the iron burn, producing sulphur dioxide and iron oxide. If a kiln is used, it is built on a slant and rotates so that the pyrites entering at the raised end drifts slowly to the lower end.

In both systems, the resulting gas is about 7 per cent sulphur dioxide, the rest being mostly oxygen, nitrogen, and





A kiln such as those used for  
extracting sulphur dioxide from  
iron pyrites and anhydrite.  
*I.C.I.*





A section of an anhydrite mine.  
*I.C.I.*





impurities such as arsenious oxide and chlorides. If the gas is to be used in the contact process it must be purified. First the heavy dust is allowed to settle from the gas. Then the gas passes electrodes so as to remove the remaining particles electrostatically. The gas is cooled and washed to remove condensable impurities and finally it is dried by being passed up a tower down which sulphuric acid flows. The gas can now be used for contact process production of sulphuric acid.

*Spent oxides* – Iron oxide is used to remove hydrogen sulphide from coal gas, producer gas, and water gas. The gas passes through the iron oxide and iron (II) sulphide and sulphur are formed. When the iron oxide mixture contains more than 50 per cent free sulphur it is replaced with fresh iron oxide.

The spent oxide is then processed and the sulphur extracted. It is burnt in a furnace like the one used in sulphur extraction from pyrites. The iron oxide is raked down from shelf to shelf and sulphur dioxide is liberated. The spent oxide now becomes iron oxide and can be treated and used again for purification of gas. The sulphur dioxide is treated to remove dust, as in the case of sulphur dioxide from iron pyrites.

*Anhydrite* – Anhydrite is calcium sulphate ( $\text{CaSO}_4$ ). It is mined in Britain at Billingham, Co. Durham. Unless carbon is used, anhydrite breaks down only at very high temperatures. In the reaction between anhydrite and carbon, carbon dioxide and calcium sulphide are formed. The calcium sulphide then reacts with more anhydrite to produce sulphur dioxide and lime. Because the reaction is reversible, sulphur dioxide production is usually assisted by adding silicon or aluminium oxides, which combine with the lime to produce

cement clinker. Sulphur dioxide is released, and the remaining products are used in cement making. The gas released is about 9 per cent sulphur dioxide, which is purified in the same way as sulphur dioxide from iron pyrites.

*Zinc sulphide* – Zinc sulphide is mined for its zinc content, but it also contains sulphur. When the ore is roasted, its sulphur content is converted to sulphur dioxide, which can then be used in sulphuric manufacturing.

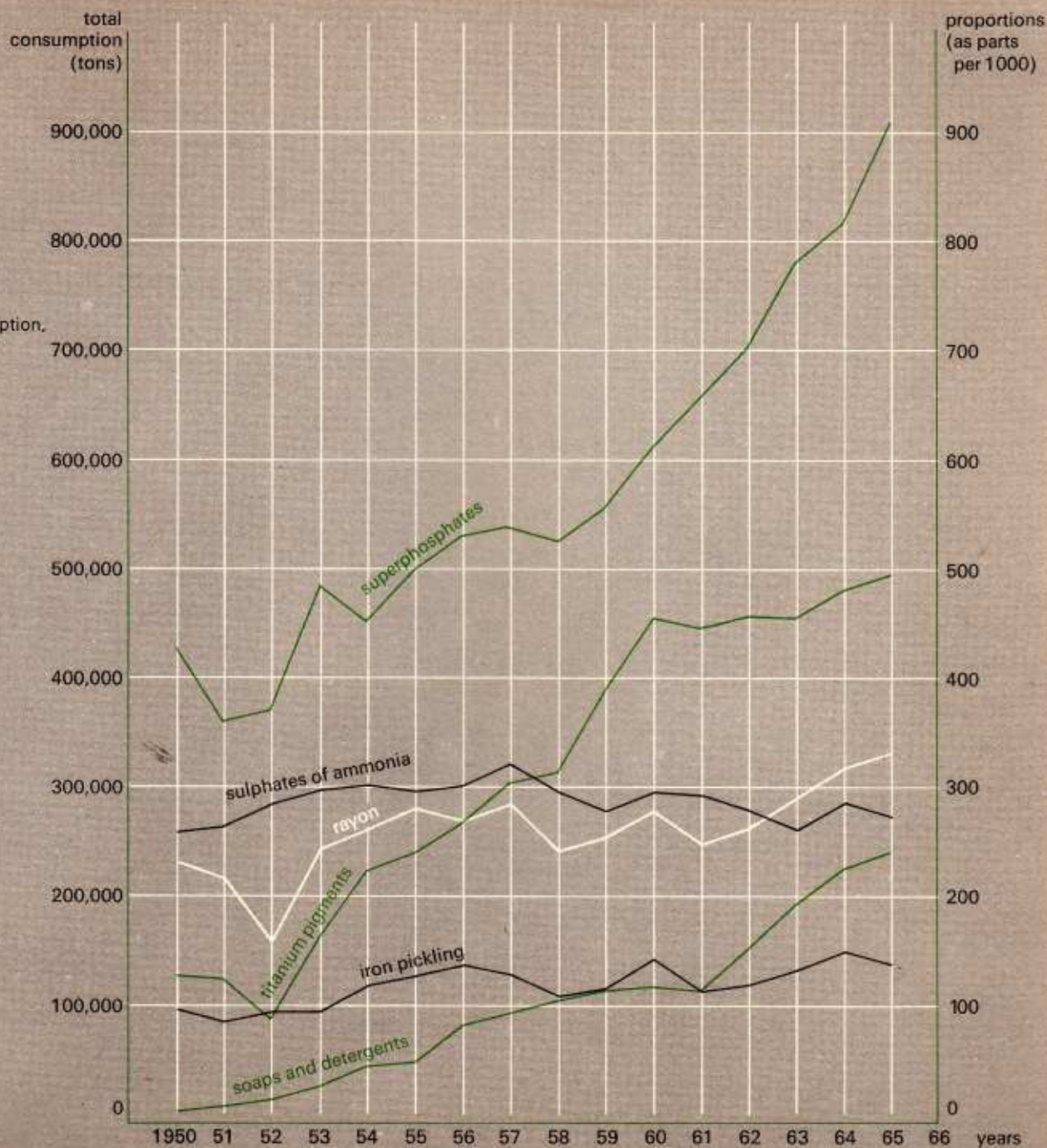
As we have seen, the degree of purity necessary for sulphuric acid depends on whether the sulphur dioxide is to be used in the contact process or in the chamber process. Purification is an extra expense, except in the case of anhydrite, whose by-product is sold to cement manufacturers. Manufacturers who use the contact process prefer to have as pure a raw material as possible. The purest of the possible raw materials is mined sulphur. More than half the sulphur dioxide used in sulphuric acid manufacturing comes from mined sulphur. Almost all this comes from the Texas deposits in the U.S.A.

Estimates are that the present deposits of pure sulphur will be exhausted by the end of the century. Some sulphuric manufacturers are already exploiting other sources, particularly anhydrite and pyrites, which now account for about a fourth of sulphur resources used in sulphuric manufacturing. Eventually, however, with all sulphur resources continuously diminishing, it will be necessary to replace sulphuric acid and sulphur products with other substances which perform the same jobs just as well. Very little time has been spent so far on developing such substances.



# Part 4 Uses

Sulphuric acid consumption,  
1950 – 1965.



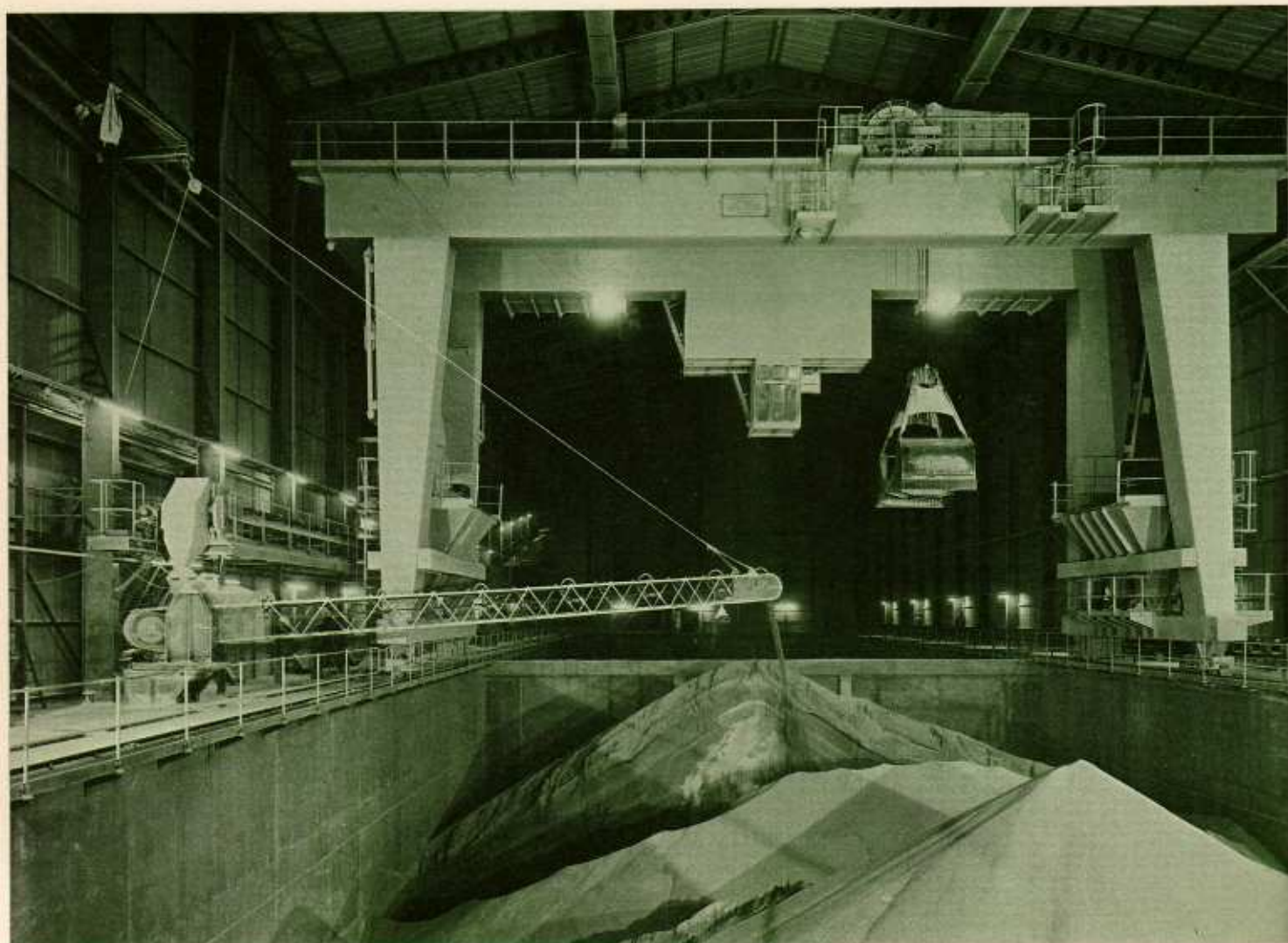


Sulphuric acid has a number of very special qualities which make it especially useful for many manufacturing processes. It is also cheaper than other substances with these properties and so all the more useful to manufacturers.

Perhaps its most useful property is its great affinity for water. It is an extremely powerful dehydrating agent.

*Rayon manufacturing* – Rayon is a fibre developed to be an inexpensive substitute for silk. Sulphuric acid is essential in

A superphosphate plant.  
*I.C.I.*





its manufacture. Rayon is made from cellulose, a substance found in wood pulp. Cellulose is treated with caustic soda (sodium hydroxide) and dried. This is treated with carbon disulphide to make a thick yellow substance called cellulose xanthate, which is then dissolved in a dilute solution of caustic soda. The solution is pumped under pressure through spinnerets, nozzles with many very fine holes. It goes into a sulphuric acid bath where the cellulose xanthate is neutralized and cellulose is reformed into a tough fibre. The excess caustic soda is neutralized with sulphuric acid, forming sodium sulphate and water. (See Background Book, *Man-Made Fibres*.)

**Fertilizers** – The largest single consumer of sulphuric acid is the superphosphate industry. In 1840 Justus von Liebig, a German chemist, demonstrated that calcium phosphate in dried bones could be supplied as a fertilizer to plants. If the bones were treated with sulphuric acid, water soluble calcium dihydrogen phosphate was formed. Plants more readily accept phosphate from this soluble compound than from insoluble calcium phosphate.

John Bennet Lawes carried on von Liebig's research, and eventually developed a process for commercial production of calcium dihydrogen phosphate, or 'superphosphate'. Mined calcium phosphate was treated with sulphuric acid to form calcium superphosphate:



A superphosphate factory began production at Ipswich in 1854.

Ammonium sulphate is another fertilizer made from sulphuric acid. It supplies nitrogen to plants. Although much is now made directly from synthetic ammonia and calcium sulphate, large quantities still come from extraction of ammonia from coke ovens and gas works. It is extracted with sulphuric acid. (See Background Book on *Fertilizers and Farm Chemicals*.)

**Pickling of metals** – Almost all iron and steel products require a coating to protect them from rust. One way of protecting them is to coat them with a substance which does not deteriorate in contact with air. Before galvanizing, plating, or enamelling can take place, the iron oxide must be completely removed from the metal's surface. Sulphuric acid is used to



Fertilizer manufacturing is still the largest single consumer of sulphuric acid.  
*Radio Times Hulton Picture Library.*



pickle the metals – to remove the oxides before the protective coating is put on. (See Background Book *Corrosion*.)

**Detergents** – Detergents and shampoos are usually made by treating by-products of petroleum refining with sulphuric acid. The most frequent kind of detergent is made from a hydrocarbon which contains a benzene ring. A hydrocarbon chain of ten to eighteen carbon atoms is attached to a benzene ring. The benzene ring is then sulphonated, a hydrogen atom being replaced by a  $-\text{SO}_3\text{H}$  group from sulphuric acid. This is treated with caustic soda, and the sodium salt of the sulphonated benzene compound is formed. The head of this molecule (the sulphonated benzene ring) is then soluble in water, while the tail, which is not soluble in water, is attracted to dirt, oils, and grease.

Today the hydrocarbon ( $\text{R} - \text{C}_6\text{H}_4$ , where R represents the hydrocarbon chain, or tail, of the hydrocarbon) is mixed with oleum. Oleum is formed by dissolving  $\text{SO}_3$  in 100 per cent sulphuric acid to produce  $\text{H}_2\text{S}_2\text{O}_7$ . The mixture of hydrocarbon and oleum produces a sulphonated hydrocarbon ( $\text{R} - \text{C}_6\text{H}_4 - \text{SO}_3\text{H}$ ) and sulphuric acid. Water is added to dilute the sulphuric acid, which is then removed. Caustic soda is then used to neutralize the sulphonated hydrocarbon to produce its sodium salt ( $\text{R} - \text{C}_6\text{H}_4 - \text{SO}_3\text{Na}$ ). The salt is mixed with other ingredients and sprayed into a drying tower. Hot air rising in the tower dries out the mixture, which falls to the bottom as granules of washing powder.

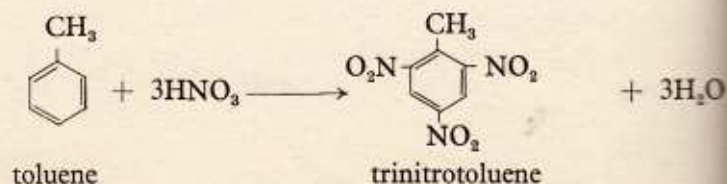
**Titanium pigments** – Titanium is a light metal which withstands high temperatures without corroding. It is used to make the outer shell of rockets and artificial satellites because

it can resist the high temperatures caused by friction with the atmosphere.

It is obtained from an ore called ilmenite, which was originally mined in Norway and is now mined in Brazil, U.S.A., West Africa, India, and Australia. Ilmenite is a mixture of iron oxide and titanium oxide. To separate the titanium from the iron, the ore is soaked in sulphuric acid. Iron sulphate and titanyl sulphate are formed. When the solution is cooled and evaporated, the iron (II) sulphate crystallizes and one is left with a fairly pure solution of titanyl sulphate. This is boiled to produce sulphuric acid and titanium hydrate. The titanium hydrate is heated to about  $1000^\circ\text{C}$  and becomes titanium oxide, a white powder used in pigment manufacturing.

**Explosives** – Nitroglycerine and trinitrotoluene manufacturers use a mixture of concentrated nitric acid and concentrated sulphuric acid.

In TNT manufacture, three hydrogen atoms in a toluene molecule are replaced by  $-\text{NO}_2$  groups from nitric acid.



The process will not take place without sulphuric acid, which both participates in the reaction mechanism and acts as a dehydrating agent.

In nitroglycerine:

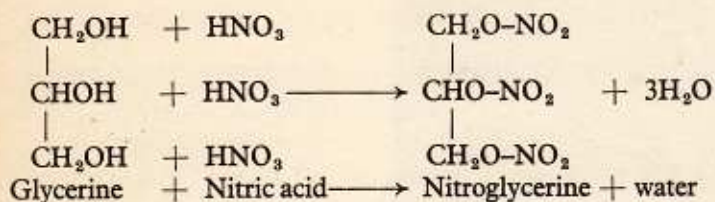




White titanium pigment production; the pigment is scraped off the roller and then passed by conveyor belt to the dryers.  
*Laporte Industries Ltd.*



TNT explosion in a quarry.  
I.C.I.



Sulphuric acid aids the process by absorbing the water produced.

Such explosives, aside from their destructive uses in military activity, are valuable in mining coal and metals, and quarrying stone. Recently they have largely been replaced by other explosives which are not produced with sulphuric acid. (See Background Book, *The Nitrogen Problem*.)

Sulphuric acid is extremely important in manufacturing dyestuffs and plastics, and in leather tanning. It is also very useful in making other acids, such as chromic acid, formic acid, tartaric acid, and hydrochloric acid. Today most hydrochloric acid is made by combining hydrogen and chlorine directly, but large quantities are still made by reacting salt and sulphuric acid to form sodium sulphate and hydrochloric acid.

In recent years superphosphate production has remained the largest single user of sulphuric acid, but since 1956 the second largest users are the producers of titanium dioxide. In Great Britain, superphosphates, titanium, sulphate of ammonia, rayon, and detergent manufacturers account for 67 per cent (or 2.2 million tons) of sulphuric consumption. The manufacture of explosives, which in 1952 consumed more than 24,000 tons of sulphuric acid, today consumes less than 11,000 tons.

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